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Approaches to Macrocyclic Polystannanes

by

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**20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)***

This report details progress towards the synthesis of macrocyclic polystannanes. Two classes of compounds containing either diphenyltin or dimethyltin atoms are being prepared. The general approach involves building the macrocycles through a series of reactions which will permit modifications in size or functional groups. The initial targets are macrocycles containing four tin atoms.

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Approaches to Macrocyclic Polystannanes

Although there are numerous applications of neutral, basic macrocyclic
compounds as cation-complexing agents, there are no reports of the appli-
cation of neutral, acidic macrocycles as anion complexing agents. This work
is directed at developing techniques for the synthesis of macrocyclic
polystannanes and the application of these compounds as anion complexing
species. The approach we have taken to this problem involves building
the macrocles in a series of reaction by methods which will allow size
and functional group modifications of the macrocycles. The initial targets
are macrocycles containing four diphenytin or dimethyltin atoms.

Progress Towards Macrocycles Containing Diphenyltins

Our effort directed toward the synthesis of phenyl-containing macro-
cyclic polystannanes started with the synthesis of 1,4-bis(triphenylstannyl)-
butane (1) which is analogous to the known 1,4-bis(trimethylstannyl)butane.[1]
In a nucleophilic displacement reaction, triphenylstannyllithium (from
triphenyltin chloride and lithium) reacted with 1,4-dibromobutane to give
1 in 82% yield.

$$Ph_3SnCl \xrightarrow{Li} Ph_3SnLi \xrightarrow{Br-(CH_2)_4-Br} Ph_3Sn-(CH_2)_4-SnPh_3$$

1
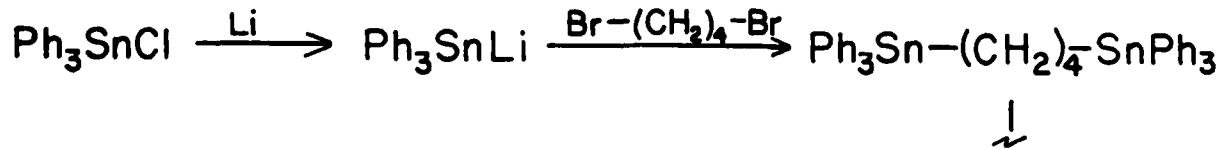
The production of $\underset{\sim}{1}$ by the "anionic" route is certainly acceptable, but we explored other methods of forming $\underset{\sim}{1}$ as model reactions for later steps in the synthesis. Compound $\underset{\sim}{1}$ may also be produced in a hydrostannation reaction since triphenyltin hydride has been shown to add to triphenyl-vinyl tin to give 1,2-bis(triphenylstannyl)ethane (eq. 1)[2] and triphenyl-3-propenyltin to give 1,3-bis(triphenylstannyl)propane (eq. 2) although in relatively low yield.[3] Experimentally, we found that 4-triphenylstannyl-1-butene ($\underset{\sim}{2}$) failed to react with triphenyltin hydride at 80 °C in 27 h.

$$Ph_3SnH + Ph_3Sn\diagup\!\!\!\!\diagdown\!\!\!\!\!\diagdown \longrightarrow Ph_3Sn-(CH_2)_2-SnPh_3 \quad (1)$$

$$Ph_3SnH + Ph_3Sn\diagup\!\!\!\!\diagdown\!\!\!\!\!\diagup\!\!\!\!\diagdown \longrightarrow Ph_3Sn-(CH_2)_3-SnPh_3 \quad (2)$$
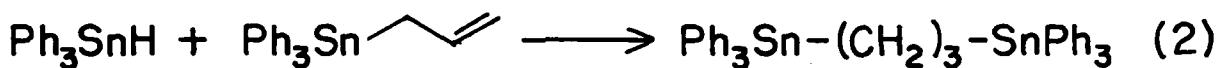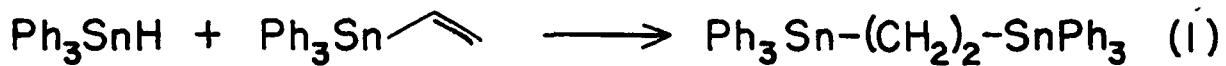
However, when azobisisobutylnitrile (AIBN) was added as a catalyst, the reaction proceeded smoothly to give $\underset{\sim}{1}$ in quantitative yield in 60 h at 90 °C.

$$Ph_3Sn\diagup\!\!\!\!\diagdown\!\!\!\!\!\diagup\!\!\!\!\diagdown + Ph_3SnH \xrightarrow{\text{AIBN}} \underset{\sim}{1}$$

$$\underset{\sim}{2}$$
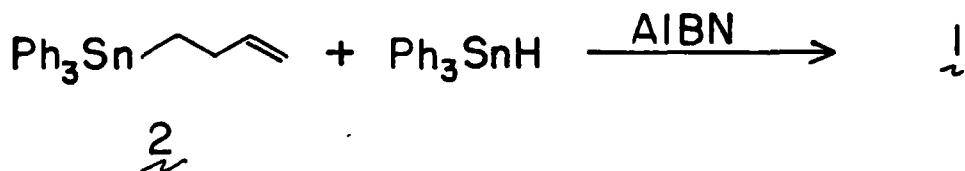
The next step in our sequence required the monofunctionalization of each of the tin atoms in $\underset{\sim}{1}$ to give the dibromide $\underset{\sim}{3}$. Again the analogous

$$Ph_3Sn-(CH_2)_4-SnPh_3 \longrightarrow Ph_2BrSn-(CH_2)_4-SnBrPh_2$$

$$\underset{\sim}{1} \qquad\qquad\qquad\qquad \underset{\sim}{3}$$

1,4-bis(bromodimethylstannyl)butane has been made by treatment of 1,4-bis(trimethylstannyl)butane with bromine in carbon tetrachloride (eq. 3).[1]

$$Me_3Sn-(CH_2)_4-SnMe_3 + Br_2 \longrightarrow Me_2BrSn-(CH_2)_4-SnBrMe_2 \quad (3)$$

We have found that, unlike the methyl case, the phenyl groups bonded to tin are so reactive that several bromination reactions do not give mono-bromo tin species but proceed readily to produce dibromo substituted tins.

Model studies for the conversion of $\underset{\sim}{1}$ to $\underset{\sim}{3}$ employed the known n-butyl-triphenyltin ($\underset{\sim}{4}$) which is readily available by several routes in high yield. In the preparation of $\underset{\sim}{4}$ we investigated a deprotonation route to triphenylstannyllithium which is patterned after the procedure recently reported by Still for conversion of tri-n-butyltin hydride to tri-n-butyl-stannyllithium by treatment with lithium diisopropylamide (LDA).[4] When triphenyltin hydride (produced in 75% yield from triphenyltin chloride by lithium aluminum hydride reduction) was treated with LDA under Still's conditions and the reaction mixture was subsequently treated with

1-chlorobutane, the desired product 4 was obtained in 90% yield. For comparison, triphenylstannyllithium prepared directly from triphenyltin chloride reacted with 1-chlorobutane to give 4 in comparable (83%) yield,

$$Ph_3SnH \xrightarrow{LDA} Ph_3SnLi \xrightarrow[90\%]{n-BuCl} Ph_3SnBu$$
$$4$$

$$Ph_3SnCl \xrightarrow{Li} Ph_3SnLi \xrightarrow[83\%]{n-BuCl} 4$$
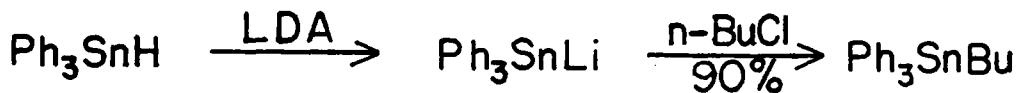
$$(Ph_3Sn)_2O \xrightarrow[44\%]{n-BuLi} 4$$
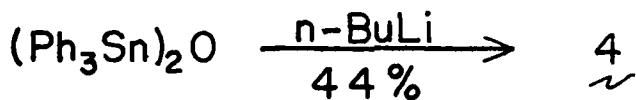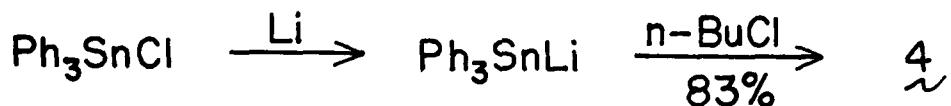
but purification of the product was much easier in the former reaction. A third preparation of 4, from the reaction of bis(triphenylstannyl)oxide with n-butyllithium was inferior.

Our initial attempts to monofunctionalize triphenylalkyltin atoms was made on the ditin compound 1. Treatment of 1 with bromine under conventional conditions[1] (-10 °C, CCl₄) gave a complicated mixture of products which was not purified. Changing the solvent to methylene chloride and lowering the reaction temperature to -78 °C failed to give better results.

We then turned to the model compound 4 and studied various bromination conditions. Treatment of 4 with bromine in carbon tetrachloride

has been reported to give monobromide $\underset{\sim}{5}$ in 63% yield after distillation.[5]
However, our attempts to brominate $\underset{\sim}{4}$ with bromine at temperatures as low

$$Ph_3SnBu \xrightarrow{\ Br_2/CCl_4\ } Ph_2BrSnBu$$

$$\underset{\sim}{4} \qquad\qquad\qquad \underset{\sim}{5}$$
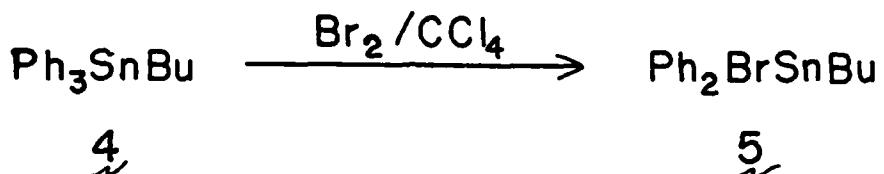
as -78 °C ($CH_2Cl_2$ solvent) led to complicated mixtures as determined by
NMR spectroscopy and TLC analysis. This behavior was similar to that
observed in the analogous bromination of $\underset{\sim}{1}$.

Krause has reported that tetraphenyltin is converted to the mono-
bromide by bromination in pyridine.[6] When we employed these conditions
for the bromination of $\underset{\sim}{4}$, we obtained monobromide $\underset{\sim}{5}$ in 60% yield. The
active brominating agent in this reaction is probably pyridine perbomide
which is used for the same type of brominations as phenyltrimethylammonium
perbromide (PTAB).[7] We found that PTAB also reacts with $\underset{\sim}{4}$ to give $\underset{\sim}{5}$ in
60% yield.

Use of the bromine/pyridine conditions for bromination of $\underset{\sim}{1}$ was
somewhat encouraging; the product mixture appeared to contain some of
the desired product by NMR spectroscopy. However, this method was
abandoned when other procedures proved to be more useful. Treatment of
$\underset{\sim}{1}$ with PTAB gave the desired $\underset{\sim}{3}$ in 70% yield, but the product was some-
what difficult to purify from bromobenzene formed as a by-product.

$$Ph_3Sn-(CH_2)_4-SnPh_3 \xrightarrow[\text{or}]{\begin{array}{c}\text{PTAB (70\%)}\\\text{HBr (100\%)}\end{array}} Ph_2BrSn-(CH_2)_4-SnBrPh_2$$

$$\underset{\tilde{}}{1} \qquad\qquad\qquad\qquad\qquad\qquad \underset{\tilde{}}{3}$$
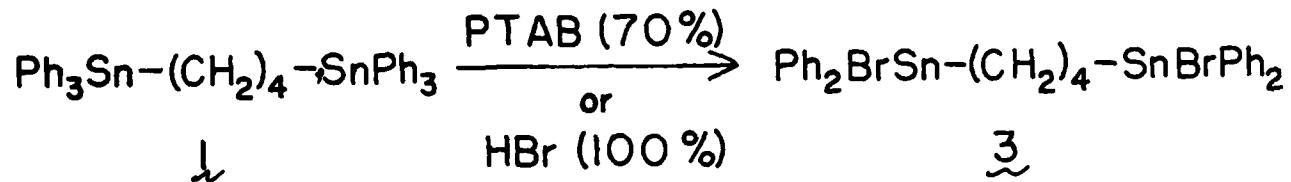
Treatment of $\underset{\tilde{}}{1}$ with gaseous HBr at 0 °C with a short contact time gave $\underset{\tilde{}}{3}$ in essentially quantitative yield; since benzene is the by-product in this reaction, purification of $\underset{\tilde{}}{3}$ was simple.

From bis(bromodiphenylstannyl)butane ($\underset{\tilde{}}{3}$) there are three strategies which could be employed in forming a macrocycle precursor. Nucleophilic displacement of halogen on tin with carbanionic species would permit the use of $\underset{\tilde{}}{3}$ directly. Conversion of $\underset{\tilde{}}{3}$ to a dilithio species (either directly or via the di-hydride) and subsequent treatment with an organic halide is another possibility. Finally conversion of $\underset{\tilde{}}{3}$ to a dihydride and reaction of this species with an olefin is possible.

In a model system reaction we found that n-butyldiphenyltin bromide ($\underset{\tilde{}}{5}$) could be converted into the corresponding hydride ($\underset{\tilde{}}{6}$) by reduction with lithium aluminum hydride (LAH). Subsequent deprotonation of $\underset{\tilde{}}{6}$ with

$$\underset{\tilde{}}{5} \xrightarrow{\text{LAH}} Ph_2HSnBu \xrightarrow[\text{2)Br}\diagdown\diagdown]{\text{1) LDA}} Ph_2SnBu$$

$$\underset{\tilde{}}{6} \qquad\qquad\qquad \underset{\tilde{}}{7}$$
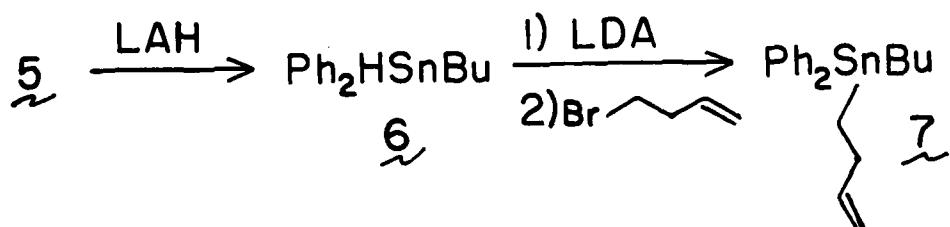
LDA followed by treatment with 4-bromo-1-butene gave the desired alkylated product 7 in modest yield.

Despite our sucess with the model system, we have as yet been unable to convert 3 to the corresponding dihydride (8) under mild LAH reaction conditions. Attempts to effect this conversion are continuing. Since bis(diphenylhydridostannyl)butane (8) was not readily available, we attempted the direct reaction of dihalide 3 with the Grignard reagent from 4-bromo-1-butene. This reaction gave the desired substitution product 9 in 77% yield.

$$3 \xrightarrow{\text{2 BrMg} \diagup \diagdown \diagdown} Ph_2Sn-(CH_2)_4-SnPh_2$$

9
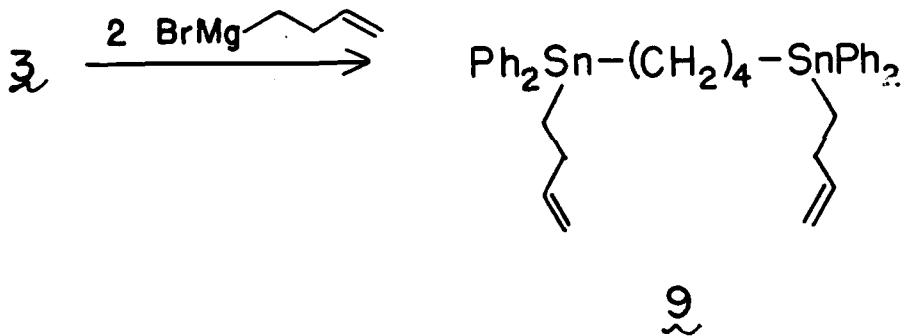
Compound 9 may be converted to a macrocycle by two different routes. Addition of the, as yet unavailable, dihydride 8 may give a 20-membered ring macrocycle directly in a double hydrostannation reaction. Alternatively

$$9 + Ph_2HSn-(CH_2)_4-SnHPh_2 \longrightarrow$$

8

$$\begin{array}{cc} Ph_2Sn-(CH_2)_4-SnPh_2 \\ | \qquad\qquad | \\ (CH_2)_4 \qquad (CH_2)_4 \\ | \qquad\qquad | \\ Ph_2Sn-(CH_2)_4-SnPh_2 \end{array}$$
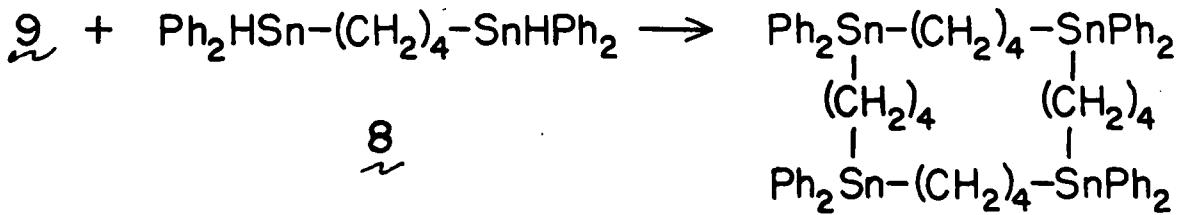
addition of functionalizable tin atoms to each terminus of $9$ is possible.
For example the reaction of $9$ with 2 equivalents of chlorodiphenyltin
hydride could give $10$ which may react with a di-Grignard reagent to give

$$9 \; + \; Ph_2SnClH \; \longrightarrow \; \begin{array}{ccc} Ph_2Sn-(CH_2)_4-SnPh_2 \\ | \qquad\qquad | \\ (CH_2)_4 \qquad (CH_2)_4 \\ | \qquad\qquad | \\ Ph_2SnCl \qquad ClSnPh_2 \end{array}$$

$$10$$
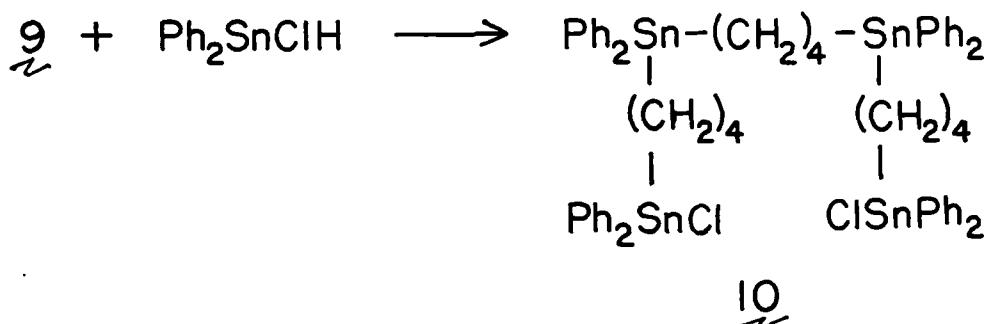
a macrocycle. Both of these approaches have been investigated briefly
in model systems. As a model for the former approach, compound $7$ was
treated with hydride $6$ under normal hydrostannation conditions, however,
we observed no reaction. As a model for the latter approach compound $7$

$$Ph_2BuSn \diagup\!\diagdown\!\diagup\!\diagdown\!\!\!\!\diagdown \qquad + \qquad Ph_2BuSnH \; \longrightarrow$$

$$7$$
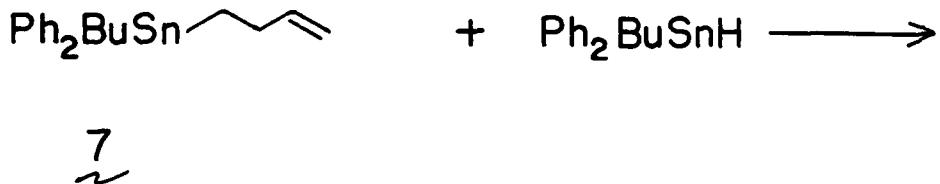
was treated with chlorodiphenyltin hydride, prepared by the redistribution
reaction between diphenyltin dichloride and tri-n-butyltin hydride.

$$Ph_2BuSn\diagup\diagdown\diagup\diagdown\quad + \quad Ph_2SnClH \quad\longrightarrow$$

$$\underset{\sim}{7}$$

Analysis of the product mixture was difficult in this case due to tri-n-butyltin chloride carried through from the preparation of the hydride. Work on both of the model reactions is continuing.

Progress Towards Macrocycles Containing Dimethyltins

Our efforts directed towards the synthesis of dimethylstannyl macrocycles have followed a pattern similar to that described above for the diphenylstannyl macrocycles. Primarily, we have attempted to develop stepwise syntheses of the macrocycles.

Several bis(trimethylstannyl) alkanes ($\underset{\sim}{11}$, n = 3,4,5) were prepared by known methods.[1] By reported procedures[1] compounds $\underset{\sim}{11}$ were brominated

$$Me_3Sn-(CH_2)_n-SnMe_3 \quad\longrightarrow\quad Me_2BrSn-(CH_2)_n-SnBrMe_2$$
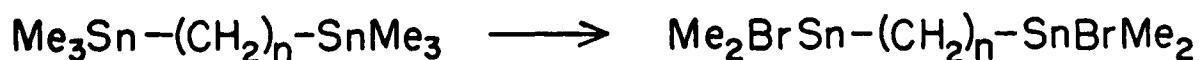
$$\underset{\sim}{11} \qquad\qquad\qquad\qquad \underset{\sim}{12}$$

to give the bis(bromodimethylstannyl) alkanes (12, n = 3,4,5). Treatment

of the compounds 12 with the mono-Grignard reagent from 1-bromo-4-chloro-

butane gave the extended acycles (13) in modest yield. Compounds 13 were

$$12 + BrMg-(CH_2)_4-Cl \longrightarrow Me_2Sn-(CH_2)_n-SnMe_2$$
$$\underset{(CH_2)_4}{|} \qquad \underset{(CH_2)_4}{|}$$
$$\underset{Cl}{|} \qquad \underset{Cl}{|}$$

$$13$$
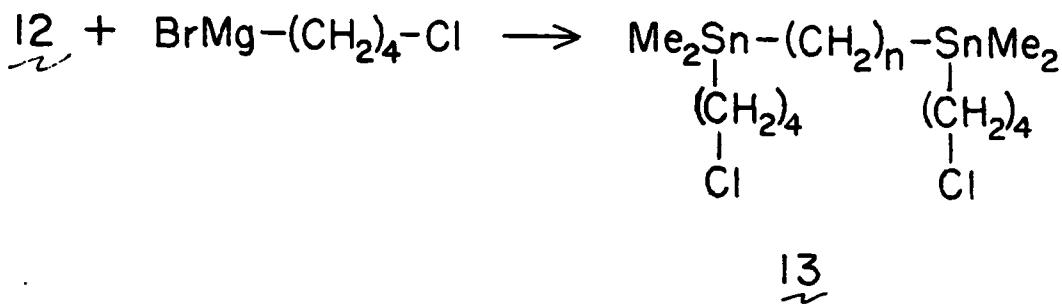
somewhat difficult to purify and, we have found, also somewhat difficult

to characterize.

Compounds 13 could be used directly in an attempted synthesis of a

macrocycle if they were treated with a bis(stannyllithium) alkane. We

have attempted this type of reaction, but have found that we cannot readily

purify products. Because of these difficulties we have developed a more

circuitous but more general approach for the further embellishment of the

macrocycle precursor.

Bromination of dimethyldiphenyltin gives dimethylphenyltin bromide

(14) which upon treatment with lithium gives the corresponding lithium

$$Ph_2SnMe_2 \xrightarrow{Br_2} PhBrSnMe_2 \xrightarrow{Li} PhSnMe_2Li$$

$$14 \qquad\qquad\qquad 15$$
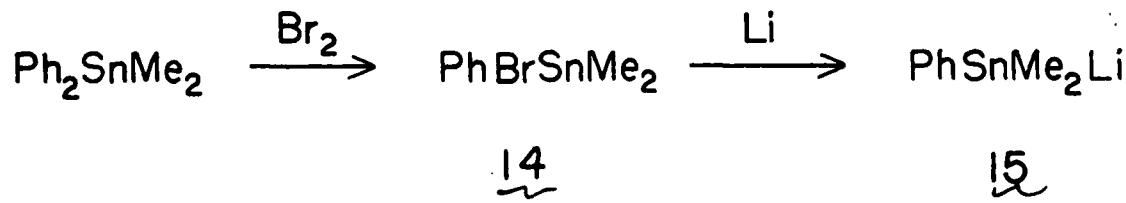
reagent 15. Treatment of compounds 13 with reagent 15 gives tetrastanna

compounds 16 in reasonable yield. Compounds 16 may be halogenated

$$13 \;+\; 15 \;\longrightarrow\; \begin{array}{c} Me_2Sn-(CH_2)_n-SnMe_2 \\ | \qquad\qquad | \\ (CH_2)_4 \qquad (CH_2)_4 \\ | \qquad\qquad | \\ Me_2SnPh \qquad PhSnMe_2 \end{array}$$
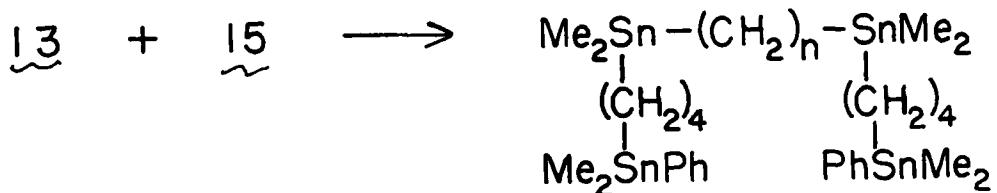
16

selectively with relative ease since the tin-aryl bonds are cleaved more

readily than tin-alkyl bonds. Essentially application of this synthetic

sequence permits us to incorporate activated tin atoms into the macro-

cycle precursor. This strategy may be easily applied to the synthesis of

a macrocycle which contains more than four tin atoms.

Treatment of 16 (n = 4) with bromine apparently gave the desired

dibromide 17 in nearly quantitative yield, but complete characterization

of 17 has not been accomplished. Treatment of 17 with the di-Grignard

reagent from 1,4-dibromobutane appeared to give the desired macrocycle

18 which has not yet been purified or completely characterized.

$$16\,(n = 4) \;\longrightarrow\; \begin{array}{c} Me_2Sn-(CH_2)_4-SnMe_2 \\ | \qquad\qquad | \\ (CH_2)_4 \qquad (CH_2)_4 \\ | \qquad\qquad | \\ Me_2SnBr \qquad BrSnMe_2 \end{array} \;\longrightarrow\; \begin{array}{c} Me_2Sn-(CH_2)_4-SnMe_2 \\ | \qquad\qquad | \\ (CH_2)_4 \qquad (CH_2)_4 \\ | \qquad\qquad | \\ Me_2Sn-(CH_2)_4-SnMe_2 \end{array}$$
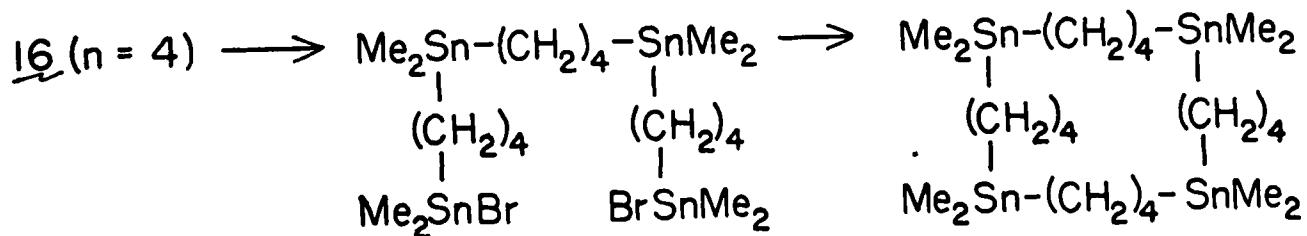
17               18

An alternative approach to simple macrocyclic polystannanes employs a "shotgun" reaction which, for the tetrastanna macrocycles involves four components reacting to give the desired macrocycle. We have attempted such reactions, but the mixture of products formed makes purification and identification of products quite difficult. Thus, for example, reaction of the dilithium reagent $\underset{\sim}{19}$ with 1,4-dibromobutane and with 1,5-dibromo-pentane gave mixtures which may contain the desired macrocycles but which

$$Me_2LiSn-(CH_2)_5-SnLiMe_2 \;+\; Br-(CH_2)_n-Br \;\longrightarrow$$

$$\underset{\sim}{19} \qquad\qquad n=4,\,5$$
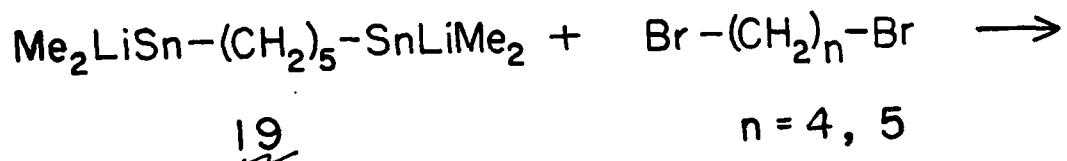
have not yet been completely purified.

EXPERIMENTAL SECTION

General. All reactions involving organometal species were run under an inert atmosphere (nitrogen or argon) using syringe transfers. ^{1}H-NMR spectra were recorded on a Varian T-60 spectrometer, and ^{13}C-NMR spectra were recorded on a JEOL PFT-100 spectrometer. Unless noted all chemical shifts are reported in ppm relative to internal $Me_4Si$. Infrared spectra were recorded on a Perkin Elmer model 297 IR spectrophotometer. Molecular weight determinations were made on a Hewlitt Packard model 302B Vapor Pressure Osmometer. Tetrahydrofuran (THF) was distilled from a purple solution of sodium-benzophenone immediately before use. The molarities of Grignard and lithium reagents were determined by quenching an aliquot with water and subsequent titration with 0.1N HCl or by direct titration of an aliquot with standardized n-butanol in xylene employing phenanthroline as an indicator.

1,3-Dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane, and 1-bromo-4-chlorobutane (Aldrich) were used without further purification. Grignard grade magnesium shavings (Fisher) were used for the preparation of all Grignard reagents. The lithium wire (PCR) contained a 1% sodium impurity and was cut into segments of 1-10 mm lengths. Anhydrous stannic chloride, tetraphenytin, and triphenyltin chloride (Alfa) were used without further purification.

Triphenyltin lithium.[1b] A solution of 5.0 g (0.013 mol) of triphenyltin chloride dissolved in 10 mL of dry THF was added to 0.9 g (0.14 g-atom) of lithium wire suspended in 15 mL of dry THF and stirred under a nitrogen atmosphere for 8 h at room temperature. The resulting dark solution was used without further treatment.

Triphenyltin hydride was prepared by the method of Kuivila.[8] To a suspension of 0.4 g (10 mmol) of lithium aluminum hydride in 40 mL of anhydrous diethyl ether cooled to 0 °C in an ice bath under a nitrogen atmosphere was added 10 g (26 mmol) of triphenyltin chloride in 60 mL of anhydrous diethyl ether. After 20 min of stirring at 0 °C, the mixture was stirred for 3 h at room temperature. The mixture was slowly hydrolyzed at 0 °C with water. The layers were separated and the organic layer was washed twice with cold water. The combined aqueous layers were washed with ether. The combined organic layers were dried (MgSO$_4$), the solvent was removed by evaporation, and the product was distilled from a 220 °C preheated oil bath to yield 6.9 g (76%) of triphenyltin hydride; bp 178-180 °C (1 Torr) [lit.[8] bp 168-172 °C (0.5 Torr)]; ir (neat) 1850, 1080 cm$^{-1}$.

4-Triphenylstannyl-1-butene (2). To 1.5 g (11.1 mmol) of 4-bromo-1-butene was added an equimolar amount of triphenyltin lithium in THF at room temperature. The mixture was stirred overnight at room temperature under a nitrogen atmosphere. The reaction was quenched by hydrolysis with a saturated solution of ammonium chloride. After separating the two layers, the aqueous layer was extracted twice with methylene chloride. The combined organic layers were washed with water and reduced. The white residue which remained was chromatographed on silica gel (Fisher 60 to 200 mesh) with methylene chloride elution to yield 2.1 g (47%) of 4-triphenylstannyl-1-butene; mp 94-95 °C; $^1$H-NMR (CDCl$_3$) δ 1.55 (t, J = 8, 2H), 2.51-2.65 (m, 2H), 4.7-5.1 (m, 2H), 5.5-6.1 (m, 1H), 7.0-7.6 (m, 15H); ir (nujol) 1625, 1075 cm$^{-1}$; $^{13}$C-NMR (CDCl$_3$) δ 140.9, 138.7, 137.0, 128.8, 128.4, 113.8, 30.4, 10.0.

1,4-Bis(triphenylstannyl)butane (1). A. Anion route. To 0.78 mL
(6.5 mmol) of 1,4-dibromobutane dissolved in 10 mL dry THF was added a
solution containing an equimolar amount of triphenyltin lithium in THF.
The mixture was stirred for 4 h at room temperature. The reaction was
quenched by hydrolysis with a saturated solution of ammonium chloride.
After separating the two layers, the aqueous layer was extracted three
times with methylene chloride. The combined organic layers were extracted
with water and dried ($MgSO_4$), and the solvent was removed by evaporation.
The residue was chromatographed on silica gel (Fisher 60 to 200 mesh)
with methylene chlordie elution to yield 4.91 g (81.5%) of 1,4-bis(tri-
phenylstannyl)butane; mp 221-223 °C; $^1$H-NMR ($CDCl_3$) $\delta$ 1.35-1.6 (m, 2H);
1.65-1.95 (m, 4H), 7.15-7.6 (m, 30H); ir (nujol) 1075 $cm^{-1}$; $^{13}$C-NMR ($CDCl_3$)
$\delta$ 138.9, 137.2, 129.1, 128.5, 31.3, 10.6.

B. Hydrostannation route. Sealed into a glass tube under vacuum
were 0.1 g (0.28 mmol) of triphenyltin hydride, 0.1 g (0.25 mmol) of
4-triphenylstannyl-1-butene, and 0.01 g (0.06 mmol) of azobisisobutyro-
nitrile. The mixture was heated in a sand bath for 60 h at 95-100 °C.
The product was chromatographed on silica gel (Fisher 60 to 200 mesh)
by elution with methylene chloride to yield 0.2 g (100%) of 1,4-bis(tri-
phenylstannyl)butane which was identical to material prepared by method
A above.

n-Butyltriphenyltin (4). A. Anion route. To 3.6 g (38 mmol) of
n-butyl chloride in 30 mL of dry THF was slowly added an equimolar quantity
of triphenyltin lithium in THF. After being stirred overnight at room
temperature under a nitrogen atmosphere, the reaction mixture was hydro-
lyzed with a saturated solution of ammonium chloride. The layers were
separated, and the aqueous layer extracted three times with methylene

chloride. The combined organic layers were washed with water, dried
(MgSO$_4$), and the solvent evaporated. The residue was chromatographed
on silica gel (Fisher 60 to 200 mesh) with methylene chloride elution to
yield 13.1 g (82.8%) of n-butyltriphenyltin; mp 57-58 °C (lit.[9] mp 61-
62 °C); ^{1}H-NMR (CDCl$_3$) δ 0.8-1.0 (m, 3H), 1.1-1.8 (m, 6H), 7.1-7.7 (m, 15H);
ir (nujol) 1080 cm$^{-1}$; ^{13}C-NMR (CDCl$_3$) δ 139.1, 136.3, 128.7, 128.4, 28.8,
27.3, 13.5, 10.8.

B. LDA route. A lithium diisopropylamide LDA solution was prepared
by adding 3.1 mL (5 mmol) of n-butyllithium (1.6 M in hexane) to a 0 °C
solution cf 0.8 mL (5.71 mmol) of diisopropylamine in 10 mL of THF and
stirring at 0 °C for 30 min. To this was added 1.25 mL (4.89 mmol) of
triphenyltin hydride. After 30 min at 0 °C, the solution was ready for
further use.

To the triphenyltin lithium mixture was added 0.52 mL (5 mmol) of n-butyl
chloride at 0 °C. After warming to room temperature and stirring for 6 h,
the reaction was quenched with a saturated ammonium chloride solution, the
combined organic layers were washed with a saturated sodium chloride solution
and dried over magnesium sulfate, and the solvent was evaporated to yield 1.8 g
(90%) n-butyltriphenyltin which was identical to that prepared by method A.

C. Oxide route. A solution of 5 g (0.013 mmol) of triphenyltin
chloride dissolved in 100 mL of diethyl ether was shaken with 100 mL of
5 M sodium hydroxide solution. The layers were separated, and the ether
solvent evaporated to yield 4.8 g (100%) of crude triphenyltin hydroxide
which was used without further purification; ir (nujol) 895 and 915 cm$^{-1}$.

Bis(triphenyltin)oxide was prepared by the method of Kushlefsky.[10] A solution of 4.8 g (0.13 mmol) of triphenyltin hydroxide in 150 mL of toluene was heated at reflux until no more water was being distilled (approximately 3 h) in a system equiped with a Dean-Stark water trap. The hot mixture was then filtered, and the solvent was evaporated to yield 3.8 g (88.5%) of crude bis(triphenyltin)oxide which was used without further purification; ir (nujol) 776 $cm^{-1}$.

To 3.8 g (5 mmol) of bis(triphenyltin)oxide suspended in 25 mL of anhydrous diethyl ether was added 3.3 mL (5 mmol) of n-butyllithium in hexane. After stirring at room temperature under a nitrogen atmosphere for 4 h, the mixture was filtered to remove the white precipitate. The filtrate was evaporated to give a yellowish-white solid which was recrystallized from 95% ethanol to yield 0.9 g (44%) of n-butyltriphenyltin.

n-Butyldiphenyltin bromide (5). A. Bromine/pyridine method. To a solution of 1 g (2.5 mmol) of n-butyltriphenyltin, in 8 mL of pyridine which was chilled in an ice bath, was added a solution of 0.135 mL (2.47 mmol) of bromine in 1.8 mL of pyridine which had been chilled in a dry ice-acetone bath. The mixture was stirred 45 min at 0 °C. Approximately 3 mL of sodium thiosulfate (1 N) was added and the mixture was swirled. After the solvent was evaporated there remained a viscous liquid which was dissolved in methylene chloride. The solution was extracted with 30% sodium hydroxide and the organic layer was then swirled with 10% hydrobromic acid and washed with 1:1 saturated sodium chloride, 1 N sodium thiosulfate and dried (MgSO₄). The solvent was evaporated to yield 0.6 g (60%) of n-butyldiphenyltin bromide; ^{1}H-NMR (CDCl₃) δ 0.7-1.0 (m, 3H), 1.1-1.5 (m, 4H), 1.7-1.9 (m, 2H), 7.1-7.9 (m, 10H); ir (nujol) 1075 $cm^{-1}$; ^{13}C-NMR (CDCl₃) δ 138.9, 135.8, 130.0, 128.9, 27.7, 26.7, 17.4, 13.5.

**B. PTAB method.** To 1.0 g (2.5 mmol) of n-butyltriphenyltin dissolved in 15 mL of tetrahydrofuran was added 1.0 g (2.7 mmol) of phenyltrimethyl-ammonium perbromide dissolved in 90 mL of tetrahydrofuran. The mixture was stirred for 6 h at room temperature. The reaction mixture was washed twice with a 1:1 mixture of saturated sodium chloride and 1 $\underline{N}$ sodium thiosulfate. The organic layer was dried (MgSO$_4$), and the solvent was evaporated. The viscous residue was chromatographed (Fisher 60 to 200 mesh) on silica gel with elution first with hexane and then with ether to yield 0.6 g (60%) of 5 which was identical to that prepared by method A above.

**1,4-Bis(bromodiphenylstannyl)butane (3).** **A. Bromine/carbon tetra-chloride method.** A solution containing 0.14 mL (2.6 mmol) of bromine in 4 mL of carbon tetrachloride was added dropwise to 1 g (1.3 mmol) of 1,4-bis(triphenylstannyl)butane dissolved in 10 mL of carbon tetrachloride with stirring at -10 °C in an ice-salt bath. The mixture was stirred for 30 min after completion of the bromine addition. The solvent was evaporated leaving a viscous residue which was heated to 80 °C under vacuum. The residue was chromatographed on silica gel (Fisher 60 to 200 mesh) by elution with hexane followed by ether. The ethereal solution was extracted twice with 30% sodium hydroxide solution. The resulting organic layer was stirred with aqueous hydrobromic acid and then dried (MgSO$_4$). The solvent was evaporated to leave a residue containing a mixture of products.

**B. Bromine/pyridine method.** To 1 g (1.3 mmol) of 1,4-bis(triphenyl-stannyl)butane dissolved in 15 mL of pyridine at 0 °C was added 0.19 mL of bromine in 4 mL of pyridine which had been chilled to 0 °C. The mixture was stirred for 6 h and allowed to warm to room temperature. The pyridine was evaporated and the residue was dissolved in methylene chloride. This solution was extracted with a 1:1 saturated sodium chloride, 1 $\underline{N}$ sodium thiosulfate solution and with 30% sodium hydroxide solution and then was treated with

10% hydrobromic acid. The product obtained after a conventional isolation appeared to be a mixture of compounds.

C. PTAB method. To a 0 °C solution of 1 g (2.7 mmol) of phenyltrimethylammonium perbromide in 50 mL of tetrahydrofuran was added 1 g (1.3 mmol) of 1,4-bis(triphenylstannyl)butane in 25 mL of tetrahydrofuran. The mixture was slowly warmed to room temperature and stirred for 3 h. After extraction with water, the aqueous layer was treated with brine and extracted twice with methylene chloride. The combined organic layers were dried (MgSO$_4$), the solvent was evaporated, and the residue was washed with diethyl ether to yield 0.7 g (70%) of 1,4-bis(bromodiphenylstannyl)butane; $^1$H-NMR (CDCl$_3$) $\delta$ 0.9 (m, 8H), 7.0–7.7 (m, 20H).

D. HBr method. Into a 0 °C solution of 1.0 g (1.3 mmol) of 1,4-bis-(triphenylstannyl)butane in 25 mL of methylene chloride was bubbled hydrogen bromide gas to saturate the solution. The mixture was stirred at 0 °C for 30 min, and the solvent was evaporated to yield 1.0 g (100%) of 1,4-bis(bromodiphenylstannyl)butane which was identical to that prepared by method C above.

Attempted preparation of 1,4-bis(diphenylhydridostannyl)butane (8). To a 0 °C suspension of 0.1 g (2.6 mmol) of lithium aluminum hydride in 10 mL of tetrahydrofuran was added 0.6 g (0.79 mmol) of 1,4-bis(bromodiphenylstannyl)-butane in 7 mL of tetrahydrofuran. The mixture was slowly brought to room temperature and stirred for 3 h. The mixture was hydrolyzed with 10% potassium hydroxide solution and ice water, and the organic layer was washed twice with a saturated solution of sodium chloride solution and dried (MgSO$_4$). No hydride absorbtion was present in the ir spectrum of the product mixture.

n-Butyldiphenyltin hydride (6). To 660 mg (1.72 mmol) of lithium aluminum hydride suspended in 20 mL of anhydrous ether and cooled to 0 °C was added 0.6 g (1.46 mmol) of n-butyldiphenyltin bromide in 8 mL of ether.

After stirring at 0 °C for 15 min, the mixture was heated at reflux for 2.5 h. The reaction was quenched slowly at 0 °C with water. The organic layer was washed twice with water, and the aqueous layer was extracted twice with ether. The combined organic layers were dried (MgSO$_4$) and reduced, and the product was evaporatively distilled at 160 °C (0.1 Torr) to yield 1 g (56%) of n-butyl-diphenyltin hydride; ir (neat) 1865, 1070 cm$^{-1}$.

n-Butyldiphenylstannyllithium. To 0.5 mL (3.6 mmol) of diisopropylamine in 10 mL of tetrahydrofuran at 0 °C was added 1.0 mL (3.0 mmol) of n-butyl-lithium in hexane. After stirring at 0 °C for 30 min, 1.0 g (3.0 mmol) of n-butyldiphenyltin hydride in 3 mL of tetrahydrofuran was added. The mixture was stirred at 0 °C for an additional 30 min. This solution was used in a further reaction.

4-(n-Butyldiphenylstannyl)-1-butene (7). To a tetrahydrofuran solution of n-butyldiphenylstannyllithium (3.0 mmol) was added 0.32 mL (3.2 mmol) of 4-bromo-1-butene. After stirring for 20 h, the reaction was quenched with a saturated ammonium chloride solution. The aqueous layer was extracted with methylene chloride, the combined organic layers were washed with brine and dried (MgSO$_4$), and the solvent was evaporated. The residue was chromato-graphed on silica gel (Fisher 60-200 mesh) with methylene chloride elution to yield 0.6 g (54%) of 4-n-butyldiphenylstannyl-1-butene; $^1$H-NMR (CDCl$_3$) δ 0.6-2.0 (m, 11H), 2.1-2.5 (m, 2H), 4.7-5.2 (m, 2H), 5.5-6.3 (m, 1H), 6.9-7.7 (m, 10H).

1,4-Bis(4-butenyldiphenylstannyl)butane (9). To 0.7 g (0.9 mmol) of 1,4-bis(bromodiphenylstannyl)butane in 10 mL of tetrahydrofuran was added 2.5 mL (1.9 mmol) of the Grignard reagent from 4-bromo-1-butene in tetrahydro-furan. The mixture was stirred at room temperature for 18 h. The reaction was quenched with a saturated solution of ammonium chloride. The aqueous layer was extracted twice with methylene chloride, the combined organic

layers were dried (MgSO$_4$), and the solvent was evaporated to yield 0.5 g
(77%) of 1,4-bis(1-butenyldiphenylstannyl)butane, $^1$H-NMR (CDCl$_3$) δ 0.7-
2.0 (m, 12H), 2.1-2.6 (m, 4H), 4,7-5.1 (m, 4H), 5.4-6.2 (m, 2H), 7.0-7.7
(m, 20H).

Attempted preparation of 1,4-bis(n-butyldiphenylstannyl)butane.
In a sand bath at 90 °C was heated 114 mg (0.296 mmol) of 4-n-butyldi-
phenylstannyl-1-butene, 100 mg (0.302 mmol) of n-butyldiphenyltin hydride
and 14.9 mg (0.091 mmol)of azobisisobutyronitrile for 36 h.  Ir analysis
of the product mixture indicated that no reaction had occurred.

Tetramethyltin was prepared by the procedure of Edgell and Word.[11]
Into a three-necked roundbottomed flask fitted with a condenser, pressure
equalizing funnel, and overhead stirrer was placed 55.0 g (2.26 g-atom) of
magnesium shavings and 600 mL of di-n-butyl ether.  A solution of 225.0 g
(1.59 mol) of methyl iodide (Fisher) in 150 mL of di-n-butyl ether was
added over 3-3.5 h at room temperature.  The mixture was stirred overnight
and 35 mL (77.9 g, 0.30 mol) of stannic chlorde was added dropwise over
2.5 h.  The resultant mixture was stirred overnight and then heated at
reflux for 1.5 h.  The mixture was distilled and the fraction with the
boiling range of 65-105 °C was collected.  Fractional distillation of this
fraction yielded 38 g (71%) of tetramethyltin; bp 76-78 °C [lit.[11] bp 78 °C];
$^1$H-NMR (CDCl$_3$, CH$_2$Cl$_2$ reference) δ 0.05 (s).

Trimethyltin bromide.  Tetramethyltin (97.3 g, 0.54 mol) in 150 mL
of CH$_2$Cl$_2$ was stirred at -78 °C and a solution of 89.0 g (0.55 mol) of
bromine in 150 mL of CH$_2$Cl$_2$ was added dropwise and the solvent was removed
in vacuo.  The product was fractionally distilled to yield 120.5 g (91%)
of trimethyltin bromide; bp 39 °C (2 Torr) [lit.[12] bp 165 °C]; $^1$H-NMR
(CDCl$_3$, CHCl$_3$ reference) δ 0.71 (s).

1,3-Bis(trimethylstannyl)propane ($\underline{11}$, $\underline{n}$ = 3). The procedure followed was similar to that of Tomborski, Ford, and Soloski.[1b] A solution of 49.4 g (0.20 mol) of trimethyltin bromide in 150 mL of THF was added over 2 h to a cooled (-10-0 °C) stirring suspension of 6.0 g (0.86 g-atom) of lithium wire in 150 mL of THF. The reaction was stirred for 1 h, and a 0.5 mL aliquot was titrated for total base (found 0.64 $\underline{M}$, calculated 0.67 $\underline{M}$). The green solution was transferred by cannula into a flask maintained at 0 °C and a solution of 20.5 g (0.10 mol) of 1,3-dibromopropane in 100 mL of THF was added dropwise over 0.5 h. The mixture was warmed to room temperature and hydrolyzed with 100 mL of water. The phases were separated and the aqueous phase was extracted three times with 75 mL portions of ether. The ethereal extracts were combined, dried ($MgSO_4$), and concentrated in vacuo. Fractional distillation of the crude product yielded 20.7 g (55%) of product; bp 45-47 °C (0.03 Torr) [lit.[1b] bp 60-64 °C (0.1 Torr)]; ^{1}H-NMR ($CDCl_3$, $CH_2Cl_2$ reference) $\delta$ 0.05 (s, 18H), 0.36 (t, 4H, J = 7Hz), 1.1-2.9 (m, 2H).

1,4-Bis(trimethylstannyl)butane ($\underline{11}$, $\underline{n}$ = 4). A. Trimethyltin lithium route. The procedure followed was similar to that of Tamborski, Ford, and Soloski.[1b] A stirring suspension of 7.0 g (1.0 g-atom) of lithium wire in 150 mL of THF was cooled (0 °C) and a solution of 39.0 g (0.16 mol) of trimethyltin bromide in 200 mL of THF was added dropwise over 3.5 h. The resultant green mixture was stirred at 0 °C for 3 h, and a 0.5 mL aliquot was titrated for total base (found 0.45 $\underline{M}$, calculated 0.45 $\underline{M}$). The solution was transferred by cannula to a dry flask maintained at 0 °C and a solution 9.5 mL (0.08 mol) of 1,4-dibromobutane in 100 mL of THF was added over 0.5 h. The light brown mixture was gradually warmed to

room temperature, and the solvent was removed in vacuo. The crude product
was washed with 50 mL of saturated aqueous ammonium chloride, and the
aqueous phase was extracted twice with 50 mL portions of ether. The ethereal
phases were combined, dried (MgSO₄), and concentrated in vacuo. Fractional
distillation of the residue yielded 26.3 g (85%) of 1,4-bis(trimethyl-
stannyl)butane; bp 60-66 °C (0.1 Torr) [lit.[1b] bp 74-76 °C (0.4 Torr)];
$^1$H-NMR (CDCl$_3$, CH$_2$Cl$_2$ reference) δ 0.05 (s, 18H), 0.61-1.14 (m, 4H),
1.14-1.78 (m, 4H).

B. Di-Grignard route. The procedure followed was that by Bulten and
Budding.[1a] A solution of 30 mL (0.25 mol) of 1,4-dibromobtuane in 450 mL
of THF was added over 3 h to 75.0 g (3.1 g-atom) of magnesium shavings
in 50 mL of THF at room temperature. The solution was stirred overnight
and a 1 mL aliquot was titrated for molarity (found 0.9 M, calculated
0.99 M). The Grignard reagent, 450 mL, was transferred by cannula to a
pressure equalizing funnel and added over 1 h to a solution of 60 g
(0.25 mol) of trimethyltin bromide in 200 mL of THF. The reaction was
heated at reflux for 3 h, allowed to stand for 2 h, and heated at reflux
for an additional 2 h. The reaction mixture was treated with 150 mL of
saturated aqueous ammonium chloride solution, and the phases were separated.
The aqueous phase was extracted with three 100 mL portions of ether, and
the ethereal phases were combined, dried (MgSO₄), and concentrated in vacuo.
Fractional distillation of the residue yielded 36.7 g (79%) of 11 (n = 4)
which was identical to the material prepared by method A above.

1,5-Bis(trimethylstannyl)pentane (11, n = 5). The procedure followed
was similar to that of Tomborski, Ford, and Soloski.[1b] Trimethyltin
bromide 29.8 g (0.12 mol) in 50 mL of THF was added dropwise over 1.25 h
to a cooled (-15-0 °C) stirring suspension of 4.5 g (0.64 g-atom) of

lithium wire in 150 mL of THF. The reaction was stirred at 0 °C for 1 h

and a 0.5 mL aliquot was titrated for total base (found 0.58 $\underline{M}$, calculated

0.61 $\underline{M}$). The green solution was transferred to a dry flask maintained

at 0 °C and a solution of 8.3 mL (0.61 mol) of 1,5-dibromopentane in

50 mL of THF was added dropwise over 0.25 h. The mixture was warmed to

room temperature and treated with 100 mL of water. The layers were

separated, and the aqueous phase was extracted twice with 75 mL portions

of ether. The ethereal phases were combined, dried (MgSO$_4$), and concen-

trated $\underline{in}$ $\underline{vacuo}$. Fractional distillation of the residue yielded 20 g

(82%) of product; bp 88-93 °C (0.6 Torr) [lit.[1b] bp 87-90 °C (0.6 Torr)];

$^1$H-NMR (CDCl$_3$, CH$_2$Cl$_2$ reference) δ 0.08 (s, 18H), 0.66-1.06 (t, 4H, J = 7Hz),

1.06-2.33 (m, 6H).

1,3-Bis(bromodimethylstannyl)propane ($\underline{12}$, n = 3). A solution of

17.8 g (0.11 mol) of bromine (Fisher) in 200 mL of CH$_2$Cl$_2$ was added drop-

wise over 3 h to a cooled (-78 °C) stirring solution of 20.3 g (0.56 mol)

of 1,3-bis(trimethylstannyl)propane. The reaction was warmed to room

temperature, and the solvent was removed $\underline{in}$ $\underline{vacuo}$ to yield a crystalline

product. Recrystallization from hexane yielded 23.4 g (84%) of $\underline{12}$ (n = 3);

mp 69-70 °C; $^1$H-NMR (CDCl$_3$, CH$_2$Cl$_2$ reference) δ 0.68 (s, 12H), 1.2-1.7

(t, 4H, J = 7Hz), 1.7-2.93 (m, 2H).

1,4-Bis(bromodimethylstannyl)butane ($\underline{12}$, n = 4) was made by a procedure

similar to that of Bulten and Budding.[1a] A solution of 74.6 g (0.19 mol)

of 1,4-bis(trimethylstannyl)butane in 200 mL of CH$_2$Cl$_2$ was stirred at -78 °C

and a solution of 62.5 g (0.39 mol) of bromine (Fisher) in 100 mL of CH$_2$Cl$_2$

was added dropwise over 1.5-2 h. The reaction was warmed to room temperature

and the slovent was removed $\underline{in}$ $\underline{vacuo}$ to yield a crystalline product.

Recrystallization from hexane yielded 98 g (98%) of $\underline{12}$ (n = 4); mp 76 °C

[lit.[1a] mp 76 °C]; $^1$H-NMR (CDCl$_3$) δ 0.73 (s, 12H), 1.26-1.56 (m, 4H),
1.56-2.0 (m, 4H).

1,5-Bis(bromodimethylstannyl)pentane (12, n = 5). To a cooled (-78 °C)
solution of 20.0 g (0.05 mol) of 1,5-bis(trimethylstannyl)pentane in
200 mL of CH$_2$Cl$_2$ was added dropwise over 1 h a solution of 16 g (0.1 mol)
of bromine (Fisher) in 110 mL of CH$_2$Cl$_2$. The reaction was warmed to
room temperature, and the solvent was removed in vacuo to yield a crystal-
line product. Recrystallization from hexane yielded 26 g (98%) of 12
(n = 5); mp 45-47 °C [lit.[1a] mp 45-47 °C]; $^1$H-NMR (CDCl$_3$, CH$_2$Cl$_2$ reference).

Dimethyldiphenyltin. To a solution of 46.7 g (0.11 mol) of diphenyl-
tin dibromide in 200 mL of THF was added 85 mL of 3 M CH$_3$MgCl over 2 h. The
reaction was stirred at room temperature for 1 h and treated with 300 mL
of saturated aqueous ammonium chloride. The ethereal phase was separated,
and the aqueous phase was extracted twice with 200 mL portions of ether.
The ethereal phases were combined, dried (MgSO$_4$), and concentrated in
vacuo. Fractional distillation of the residue yielded 20.1 g (61%) of
dimethyldiphenyltin; bp 98-100 °C (0.07 Torr) [lit.[13] bp 127-140 °C
(0.3 Torr)]; $^1$H-NMR (CH$_2$Cl$_2$ reference) δ 0.68 (s, 6H), 7.24-7.78 (m, 10H).

Dimethylphenyltin bromide. A solution of 20.1 g (0.66 mol) of di-
methyldiphenyltin in 250 mL of toluene was cooled to -75 °C. A solution
of 10.6 g (0.66 mol) of bromine in 100 mL of CH$_2$Cl$_2$ was added over 2 h.
The mixture was warmed to room temperature and concentrated in vacuo.
Fractional distillation of the residue yielded 13.7 g (68%) of dimethyl-
phenyltin bromide; bp 65 °C (0.05 Torr); $^1$H-NMR (CDCl$_3$, CH$_2$Cl$_2$ reference)
δ 0.98 (s, 6H), 7.11-7.65 (m, 5H).

1,13-Dichloro-5,5,9,9-tetramethyl-5,9-distanno-tridecane (13, n = 3).
1-(4-Chlorobutyl)magnesium bromide was prepared by the procedure of Nöel,
Combret, Leroux, and Normant.[14] To a cooled (-15 to -8 °C) suspension of
1.0 g (41.5 mg-atom) of magnesium shavings 10 mL of THF was added over a
period of 1 h   a solution of 7.1 g (41.5 mmol) of 1-bromo-4-chlorobutane
in 75 mL of THF.  The solution was stirred (ca. -10 °C) until all of the
magnesium was consumed (2-3 h).  A solution of 9.5 g (19.0 mmol) of 1,3-
bis(dimethylbromostannyl)propane in 50 mL of THF was added over 0.75 h.
The reaction was warmed to room temperature and concentrated in vacuo.
The crude product was diluted with 100 mL of water, and the mixture was
extracted three times with 100 mL portions of ether.  The ethereal phases
were combined, dried (MgSO$_4$), and concentrated in vacuo to yield 8.8 g
(89%) of crude product; $^1$H-NMR (CDCl$_3$, CHCl$_3$ reference) δ 0.05 (s, 12H),
0.68-1.15 (m, 8H), 1.15-1.45 (m, 2H), 1.45-2.08 (m, 8H), 3.38-3.72 (t, 4H,
J = 6.5Hz).

1,14-Dibromo-5,5,10,10-tetramethyl-5,10-distannatetradecane (13, n = 4).
A. A solution of 4.0 g (7.8 mmol) of 1,4-bis(dimethylbromostannyl)butane
in 20 mL of THF was added dropwise over 1 h to a cool (-15-0 °C) suspension
of 0.2 g (29 mg-atom) of lithium wire in 50 mL of THF.  The green mixture
was stirred for 2 h, and a 0.5 mL aliquot was titrated for total base
(found 0.10 M, calculated 0.11 M).  The solution was transferred by cannula
to a jacketed pressure equalizing funnel maintained at -78 °C.  The solution
was added dropwise over 0.5 h to an excess of 25.0 g (115.7 mmol) of
1,4-dibromobutane which was at room temperature.  The reaction was stirred
for 15 h after which 100 mL of water were added.  The ethereal phase was
separated, and the aqueous phase was extracted twice with 100 mL portions
of solvent ether.  The ethereal phases were combined, dried (MgSO$_4$), and

concentrated <u>in vacuo</u>. Fractional distillation removed the excess 1,4-di-bromobutane, and the crude product was submitted to silica gel chromato-graphy (1" x 48" column, and hexane elution) to yield 3.0 g (66%) of 13 (n = 4); $^1$H-NMR (CDCl$_3$, CHCl$_3$ reference) δ -0.2 (s, 12H), 0.35-0.85 (m, 8H), 0.85-2.08 (m, 12H), 3.35 (t, 4H, J = 7Hz); osmometric MW: found 545, calculated 537.

<u>B.</u>  1-Bromo-4-chlorobutane(3.3 g, 19.5 mmol) in 30 mL of THF was added dropwise over 1.5 h to a cooled (-15 °C) suspension of 0.47 g (19.5 mg-atom) of magnesium shavings in 30 mL of THF. The mixture was stirred at -15 °C until all of the magnesium was consumed (5 h), and a solution of 4.4 g (8.6 mmol) of 1,4-bis(bromodimethylstannyl)butane was added over 0.25 h. The mixture was warmed to room temperature, stirred for 11 h, and heated at reflux for 1 h. The mixture was treated with 75 mL of saturated aqueous ammonium chloride, the ethereal phase was separated, and the aqueous phase was extracted twice with 50 mL of ether. The ethereal phases were combined, dried (MgSO$_4$), and concentrated <u>in vacuo</u>. Fractional distillation of the crude product yielded 3 g (67%) of 13 (n = 4); bp 165 °C (0.05 Torr).

1,15-Dichloro-5,5,11,11-tetramethyl-5,11-distannapentadecane (13, n = 5). A solution of 7.0 g (41.1 mmol) of 1-bromo-4-chlorobutane in 75 mL of THF was added dropwise over 1 h to a cooled (-10 °C) suspension of 1.0 g (41.1 mg-atom) of magnesium shavings in 75 mL of THF. The mixture was stirred at -10 °C until all the magnesium was consumed (1 h) and a solution of 9.0 g (17.0 mmol) of 1,5-bis(bromodimethylstannyl)pentane in 50 mL of THF was added dropwise over 0.5 h. The mixture was warmed to room temper-ature and treated with 50 mL of water. The phases were separated and the aqueous phase was extracted with three 100 mL portions of ether. The

ethereal phases were combined, dried (MgSO₄), and concentrated in vacuo

to yield 9.6 g (102%) of crude product. Purification by high pressure

liquid chromatography (Bio-beads SX-8 column) yielded 9.4 g (100%) of

product 13 (n = 5); ¹H-NMR (CDCl₃, CHCl₃ reference) δ 0.05 (s, 12H),

0.58-1.02 (m, 8H), 1.02-1.92 (m, 14H), 3.35-3.72 (t, 4H, J = 6.5Hz).

1,16-Diphenyl-1,1,6,6,11,11,16,16-octamethyl-1,6,11,16-tetrastanna-

hexadecane (16, n = 4). Dimethylphenyltin bromide, 14.2 g (46.4 mmol),

in 100 mL of THF was added dropwise over 2 h to a cooled (0 °C) suspension

of 6.0 g (864.0 mg-atom) of lithium wire in 200 mL of THF. The mixture

was stirred at 0 °C for 2 h, and a 0.5 mL aliquot was titrated for total

base (found 0.756 M, calculated 0.154 M). The green solution was trans-

ferred by cannula to a flask maintained at 0 °C, and a solution of 12.4 g

(23.1 mmol) of 1,14-dichloro-5,5,10,10-tetramethyl-5,10-distannatetra-

decane in 50 mL of THF was added over 0.5 h. The mixture was stirred at

0 °C for 1 h, warmed to room temperature, and treated with 75 mL of water.

The ethereal phase was separated, and the aqueous phase was extracted with

three 100 mL portions of ether. The ethereal phases were combined, dried

(MgSO₄), and concentrated in vacuo to yield 22 g of crude product. The

crude product was distilled to remove low boiling impurities and then

purified by high pressure liquid chromatography (Bio-beads SX-8 column)

to yield 11.6 g (55%) of 16 (n = 4); ¹H-NMR (CH₂Cl₂ reference) δ 0.11

(s, 12H), 0.38 (s, 12H), 0.71-1.11 (m, 8H), 1.11-1.88 (m, 12H), 7.14-7.64

(m, 10H); osmometric MW: found 850, calculated 918.

1,16-Dibromo-1,1,6,6,11,11,16,16-octamethyl-1,6,11,16-tetrastanna-

hexadecane (17). A solution of 6.6 g (41.1 mmol) of bromine in 50 mL of

CH₂Cl₂ was added dropwise over 1 h to a cooled (-78 °C) solution of 19.0 g

(20.7 mmol) of 1,16-diphenyl-1,1,6,6,11,11,16,16-octamethyl-1,6,11,16-

tetrastannahexadecane. The solution was warmed to room temperature and

the solvent was removed in vacuo. The crude product was purified by high pressure liquid chromatography (Bio-beads SX-8 column) to yield 19.3 g (100%) of 17; H-NMR ($CH_2Cl_2$ reference) δ 0.06 (s, 12H), 0.73 (s, 12H), 0.78-1.04 (m, 12H), 1.04-1.91 (m, 12H); osmometric MW: found 890, calculated 923.

Attempted synthesis of 1,1,6,6,11,11,16,16-octamethyl-1,6,11,16-tetrastannacycloeicosane. A. A solution of 4.6 g (7.4 mmol) of 1,14-dibromo-5,5,10,10-tetramethyl-5,10-distannatetradecane in 30 mL of THF was added dropwise over 1.75 h to 2.2 g (90.4 mg-atom) of magnesium shavings in 25 mL of THF. The suspension was stirred for 16 h at room temperature and transferred by cannula to a flask containing 230 mL of THF. A solution of 3.78 g (7.4 mmol) of 1,4-bis(bromodimethylstannyl)butane in 220 mL of THF was added dropwise over 8 h and the mixture was heated at reflux for 1 h. The reaction was stirred overnight and then treated with 100 mL of water. The ethereal phase was separated, and the aqueous phase was extracted with three 75 mL portions of ether. The ethereal phases were combined, dried ($MgSO_4$), and concentrated in vacuo. The crude product was submitted to high pressure liquid chromatography (Bio-beads column) and 1.1 g (18%) of product was isolated. Analysis of the product was by ^{1}H-NMR spectroscopy. Further characterization of the product was not accomplished; ^{1}H-NMR ($CDCl_3$, $CH_2Cl_2$ reference) δ 0.07 (s, 24H), 0.60-1.13 (m, 16H), 1.13-1.83 (m, 16H).

B. A solution of 9.0 g (41.8 mmol) of 1,4-dibromobutane in 50 mL of THF was added dropwise over 5 h to a suspension of 4.5 g (180.0 mg-atom) of magnesium shavings in 200 mL of THF. The mixture was stirred overnight, and 175 mL of the Grignard reagent was transferred by cannula to a round-bottomed flask fitted with a pressure equalizing funnel and a condenser.

The Grignard reagent was diluted with 300 mL of THF and a solution of 10.0 g (19.4 mmol) of 1,4-bis(dimethylbromostannyl)butane in 250 mL of THF was added dropwise over 8 h. The solution was heated at reflux for 1 h and cooled to room temperature. The solution was hydrolyzed with 200 mL of saturated aqueous ammonium chloride, and the ethereal phase was separated. The aqueous phase was extracted with three 50 mL portions of ether. The ethereal phases were combined, dried (MgSO$_4$), and concentrated in vacuo. The crude product (10.5 g) was submitted to HPLC chromatography (Bio-beads SX-12 solumn) and a mixture of products were isolated. Further attempts to purify the product were unsuccessful.

C. A solution of 5.0 g (5.4 mmol) of 1,16-dibromo-1,1,6,6,11,11,16,16-octamethyl-1,6,11,16-tetrastannahexadecane in 250 mL of THF was added dropwise over 7 h to a stirring solution of 18 mL of 0.35 M di-Grignard from 1,4-dibromobutane which was diluted with 500 mL of THF. The mixture was heated at reflux for 10 h and then stirred at room temperature for 2 h. The mixture was treated with 100 mL of saturated aqueous ammonium chloride, and the ethereal phase was separated. The aqueous phase was extracted with three 100 mL portions of ether. The ethereal phases were combined, dried (MgSO$_4$), and concentrated in vacuo. Purification on high pressure liquid chromatography (Bio-beads SX-12 column) yielded 2.5 g of product.

D. A suspension of 1.0 g (144.0 g-atom) of lithium wire in 100 mL of THF was cooled to 0 °C, and a solution of 3.5 g (6.8 mmol) of 1,4-bis-(bromodimethylstannyl)butane in 100 mL of THF was added dropwise over 1.5 h. The reaction was stirred at 0 °C for 2 h, and a 2 mL aliquot was titrated for total base (found 0.03 M, calculated 0.03 M). The green solution was transferred by cannula to a flask maintained at -78 °C and a solution of 2.9 g (5.4 mmol) of 1,14-dichloro-5,5,10,10-tetramethyl-5,10-distannatetradecane in 250 mL of THF was added over 3 h. The solution

was stirred at -78 °C for 1.5 h, warmed to room temperature, stirred for 3 h, and then treated with 100 mL of saturated aqueous ammonium chloride. The ethereal phase was separated, and the aqueous phase was extracted twice with 50 mL portions of ether. The ethereal extracts were combined, dried (MgSO$_4$), and concentrated in vacuo. Attempted purification of the crude product by high pressure liquid chromatography (Bio-beads SX-8 column) was unsuccessful.

## References

(1) (a) J. Bulten and H. A. Budding, J. Organomet. Chem., 110, 167 (1976); (b) C. Tamborski, F. Ford, and E. J. Soloski, J. Org. Chem., 28, 181 (1963).

(2) M. C. Henry and J. G. Noltes, J. Am. Chem. Soc., 82, 558 (1960).

(3) J. G. M. van der Kerk and J. G. Noltes, J. Appl. Chem., 9, 106 (1959).

(4) W. C. Still, J. Am. Chem. Soc., 100, 1481 (1978).

(5) S. D. Rosenberg, E. Debreezeni, and E. L. Weinberg, J. Am. Chem. Soc., 81, 972 (1959).

(6) E. Krause, Chem. Ber., 51, 912 (1918).

(7) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. 1, Wiley, New York, 1967, p 855.

(8) H. G. Kuivila and O. F. Beumel, J. Am. Chem. Soc., 83, 1246 (1961).

(9) H. Schumann, P, Jutz, A. Roth, P. Schwabe, and E. Schauer, J. Organomet. Chem., 10, 71 (1967).

(10) B. Kushlefsky, I. Simmons, and A. Ross, Inorg. Chem., 2, 187 (1963).

(11) W. F. Edgell and C. H. Ward, J. Am. Chem. Soc., 76, 1169 (1954).

(12) C. A. Kraus and A. M. Neal, J. Am. Chem. Soc., 51, 2403 (1929).

(13) R. H. Bullard and W. R. Robinson, J. Am. Chem. Soc., 49, 1368 (1927).

(14) M. Nöel, J. Combret, Y. Leroux, and J. Normant, C. R. Acad. Sci., Ser. B, 268, 1152 (1969).

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